1976

Utilization of Fly Ash in the Removal of Orthophosphate from Water Samples

Marla Rae Behm

UTILIZATION OF FLY ASH IN THE REMOVAL OF ORTHOPHOSPHATE FROM WATER SAMPLES

BY

MARLA RAE BEHM

A thesis submitted in partial
fulfillment of the requirements for the degree
Master of Science, Major in Chemistry
South Dakota State University

1976

UTILIZATION OF FLY ASH IN THE

REMOVAL OF ORTHOPHOSPHATE FROM WATER SAMPLES

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Science, and is acceptable for meeting the thesis requirements for this degree. Acceptance of this thesis does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Major Advisor Date

Head, Chemistry Department Date

ACKNOWLEDGEMENTS

I would like to express my deepest appreciation to the following:

To Dr. William Jensen for being there when I needed him. His guidance and encouragement throughout this project and especially his patience and availability during the writing of this thesis will always be remembered.

To the faculty and staff of Shepard Hall for the learning experiences and friendships that we shared.

To the students and staff at Mary College who have shown me that it was well worth the effort.

To my friends who were a constant source of encouragement.

To my family for letting me travel my own path, but who were always there to lean on when I needed them.

Thank you all.

MRB

TO DAD AND MOM

UTILIZATION OF FLY ASH IN THE REMOVAL OF ORTHOPHOSPHATE FROM WATER SAMPLES

Abstract

MARLA RAE BEHM

Under the supervision of Dr. William Jensen

The ability of different fly ash samples to remove orthophosphate from standard phosphate solutions and from wastewater samples is reported. The results of studies to determine the temperature, the amount of fly ash, and the time necessary for maximum orthophosphate removal are included.

The mode of action, whether by adsorption onto the fly ash or by a precipitation reaction with one or more of the soluble components from the fly ash, is also investigated.

The chemical compounds present in the fly ash, as determined by x-ray diffraction, are also included.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

In recent years the accelerated eutrophication of lakes has become a matter of wide concern. The massive algal blooms covering the lakes not only hinder the recreational aspects associated with the clear, blue lake water but more importantly they substantially lower the quality of the water rendering it unfit for use unless treated to remove the color, odor, and taste.

The amount of algae in natural waters is determined by the presence of the nutrients needed for algal growth. The nutrients required include carbon, nitrogen, hydrogen, and phosphorus as well as several other trace minerals. There has been much discussion concerning the "limiting" factor in algal growth. However, it is now recognized that successful treatment can be achieved by controlling the "key" nutrient. The key nutrient is defined as that nutrient which can be controlled with the current technology and financial resources available.

Even though this nutrient is not the limiting factor in the algal growth, it can be made the limiting factor if the concentration can be sufficiently reduced. Of all the nutrients needed for algal growth, phosphorus is that one nutrient which can be considered the key nutrient in most lakes where immediate control is needed.[1]

Although phosphorus is found in reasonable amounts in the earth's crust and is relatively abundant in soil, its movement is restricted because of its limited solubility and because it is retained by components of the soil. However, the mining of phosphate and its application in agricultural, industrial, and household uses have increased nearly

exponentially over the last few decades.[2] The flow of phosphorus from land to water has increased because of various technological measures, such as clearing land and municipal waste disposal. Once the phosphorus is present in the natural waters it may be removed and utilized temporarily for algal growth but will eventually be returned to the water upon decay of the algae. Thus the amount of phosphorus in natural waters is constantly increasing and is resulting in an ever-increasing amount of algal growth.

The other necessary nutrients which are present (mainly nitrogen and carbon) would be much more difficult to control than the phosphorus concentration. For this reason technology has been developed to lower the phosphorus concentration in wastewater before discharging it into the natural waters.

The removal of phosphate by the addition of aluminum salts is commonly used. The exact mode of action, whether by adsorption onto the precipitating aluminum hydroxides or by precipitation as the aluminum phosphate, has been the subject of much discussion. The current consensus is that the aluminum reacts with the orthophosphate to form the insoluble aluminum phosphate.[3] The removal of phosphate using iron salts has also been commonly used.[4] The addition of lime to wastewater has also been used as an efficient means of removing the phosphate.[5] In all of these precipitation reactions the exact composition of the precipitate is greatly influenced by the pH of the solution.

The addition of these chemicals to wastewater has been shown to reduce the phosphate pollution in the wastewater and is currently being used.[6] It has also been found that another common pollutant, fly ash,

contains these same chemicals.

Increasing energy demands have resulted in the construction of numerous coal-burning electrical plants. Strict environmental regulations have forced these plants to remove the particulate matter from the flue gases by use of electrostatic precipitators or dust collectors. This particulate matter, commonly known as fly ash, has itself become a pollutant. Approximately 20 million tons of fly ash were produced in the United States in 1968 and it is estimated that the annual fly ash output will reach 45 million tons by 1980.[7]

Fly ash is a heterogeneous mixture with a wide variation in physical and chemical properties. The color of fly ash ranges from light gray to dark gray. It is a very fine powder and consequently has a large surface area of approximately 5000 cm^2/cm^3.[8] The chemical analysis of a typical sample of fly ash is given in Table 1.

Fly ash exhibits pozzolanic properties and thus far the main uses of fly ash have been as a constituent in concrete and concrete-related products or as a builder in soil or roadway conditioning. It has also been shown that the large surface area and residual carbon content make fly ash an effective adsorbent material capable of removing many dissolved and suspended organic contaminants from polluted waters.[9]

As stated previously fly ash also contains the chemicals most often used to remove phosphate from wastewater. The purpose of this study was to determine how effective the fly ash would be in removing orthophosphate from standard phosphate samples and from wastewater samples. The mode of action for phosphate removal was also investigated.

It should be noted that phosphorus in natural waters may be in the

form of soluble orthophosphate, polyphosphate, insoluble inorganic phosphate, or organic phosphorus compounds. This study deals only with the soluble orthophosphate.

TABLE 1

TYPICAL ANALYSIS OF FLY ASH[10]

Material	Percent Abundance
SiO_2	41.5
Al_2O_3	11.5
Fe_2O_3	3.5
TiO_2	1.0
P_2O_5	0.3
CaO	18.4
MgO	5.7
Na_2O	4.8
K_2O	0.5
SO_3	3.7
Total	90.9

EXPERIMENTAL

PRELIMINARY PREPARATIONS: To eliminate possible phosphate contamination all glassware used throughout the project was allowed to stand for 24 hours in cleaning solution (a saturated solution of sodium dichromate in concentrated sulfuric acid), rinsed several times with distilled water, allowed to stand in distilled water for 24 hours, and finally rinsed several times with distilled water.

The distilled water used for all solutions and dilutions was deionized by passing it through a Bantam mixed-bed demineralizer column.

Three different fly ash materials were used during the project. They were used as received and are described as follows:

a) ash from lignite coal taken from Gascoyne mine, North Dakota, fired at Fergus Falls, Minnesota, power plant and collected from the electrostatic precipitators,

b) ash from the Stanton, North Dakota, power plant collected from the dust collectors,

c) ash from Big Stone, South Dakota, power plant collected from the electrostatic precipitators.

METHODS OF ORTHOPHOSPHATE ANALYSIS: The orthophosphate concentrations of the standard solutions and water samples used throughout this work were determined in terms of ppm phosphorus (or ppm P).

A standard phosphate solution was prepared by dissolving 220.0 mg of anhydrous KH_2PO_4 in sufficient water to make one liter of solution. One ml of the standard solution contained 50.0 μg phosphorus which gives a 50 ppm P solution.

Two methods for the determination of orthophosphate concentrations were tested: the ascorbic acid method[11] and the stannous chloride method.[12] Standard curves covering the range of 0.05-1.00 ppm P were prepared using both methods (Table 2, Figs. 1 and 2). The absorbance of each solution was measured using a Beckman DK-2A Spectrophotometer. After comparing the two methods the ascorbic acid method was chosen for all subsequent experiments because of the stability of the colored complex formed in this method.

TABLE 2

PREPARATION OF STANDARD CURVES

PPM P Present	Ascorbic Acid Method Average Net Absorbance λ = 882 nm	Stannous Chloride Method Average Net Absorbance λ = 690 nm
0.05	---	0.040
0.10	---	0.085
0.20	0.143	0.170
0.30	---	0.274
0.40	0.287	0.361
0.60	0.435	0.524
0.80	0.580	0.700
1.00	0.727	0.829

DETERMINATION OF CONDITIONS FOR MAXIMUM ORTHOPHOSPHATE REMOVAL: In order to determine the conditions necessary for maximum removal of orthophosphate from standard KH_2PO_4 samples the following parameters were varied: type of fly ash, amount of fly ash, and temperature of

FIGURE 1

STANDARD CURVE FOR ORTHOPHOSPHATE CONCENTRATION

(ASCORBIC ACID METHOD)

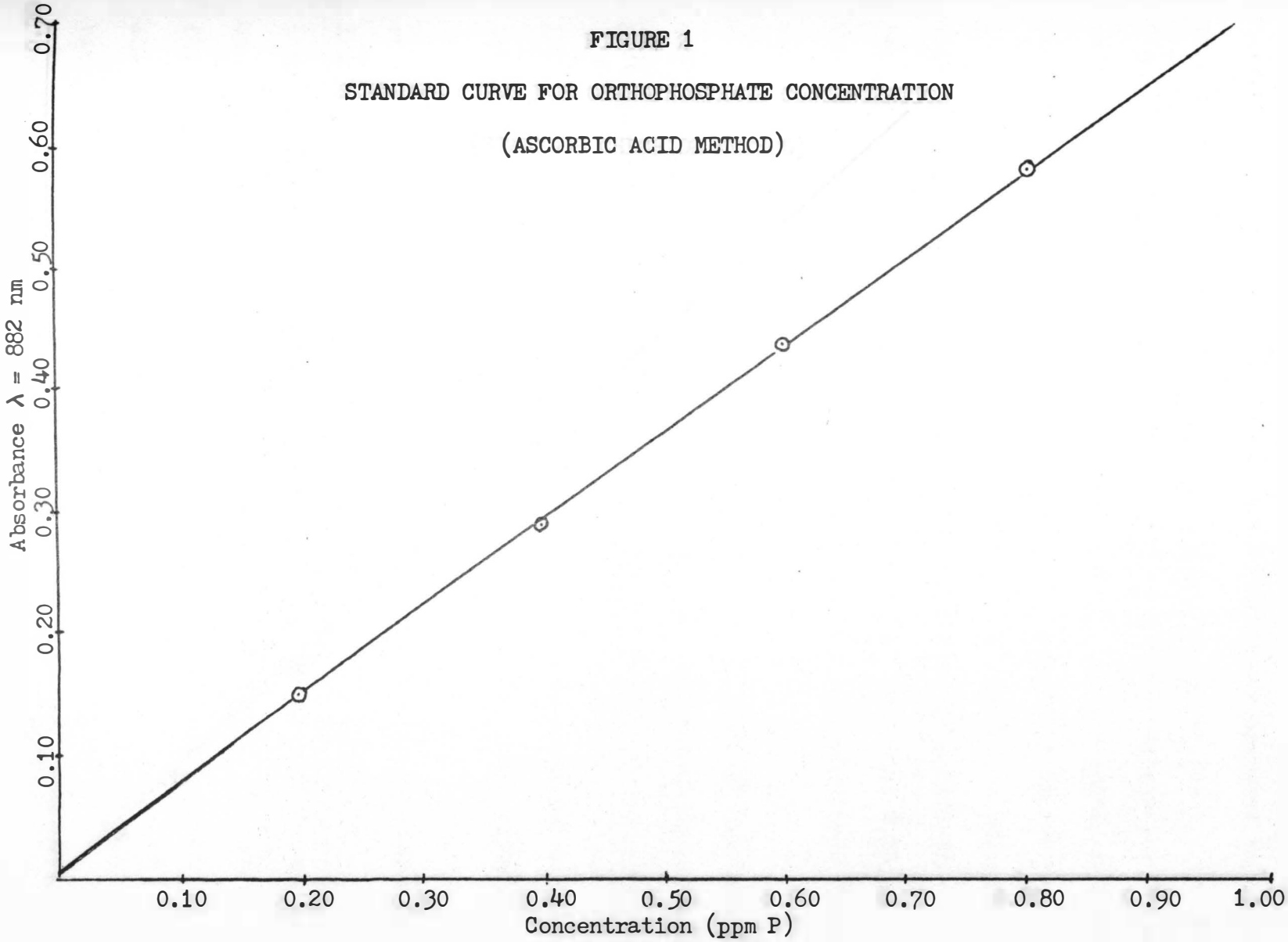
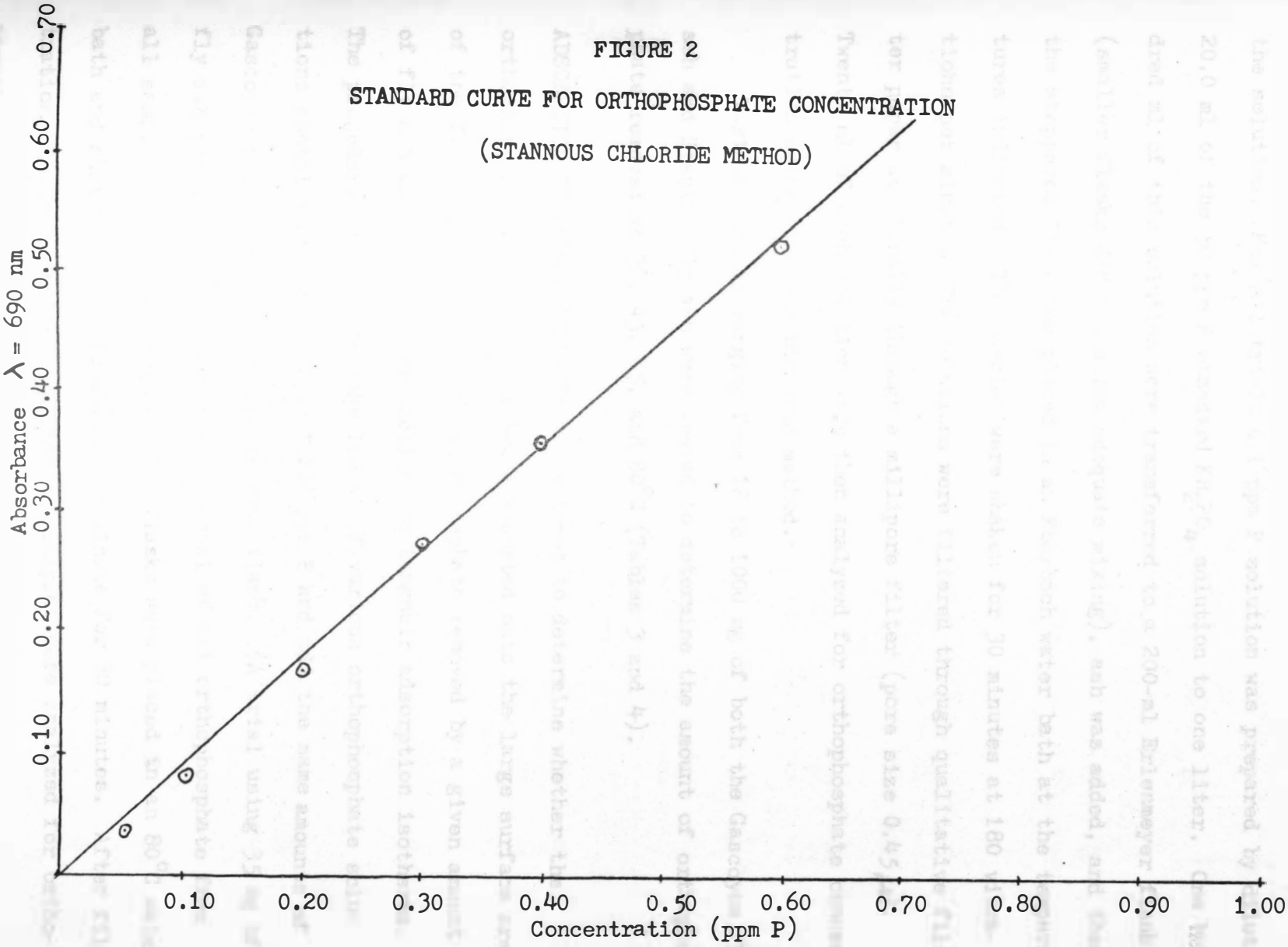


FIGURE 2

STANDARD CURVE FOR ORTHOPHOSPHATE CONCENTRATION

(STANNOUS CHLORIDE METHOD)



the solution. For all trials a 1 ppm P solution was prepared by diluting 20.0 ml of the 50 ppm P standard KH_2PO_4 solution to one liter. One hundred ml of this solution were transferred to a 200-ml Erlenmeyer flask (smaller flasks did not allow adequate mixing), ash was added, and then the stoppered flask was placed in an Eberbach water bath at the temperatures indicated. The samples were shaken for 30 minutes at 180 vibrations per minute. The solutions were filtered through qualitative filter paper and finally through a millipore filter (pore size 0.45 μ). Twenty ml of each solution were then analyzed for orthophosphate concentration using the ascorbic acid method.

Various amounts ranging from 10 to 1000 mg of both the Gascoyne fly ash and Stanton fly ash were tested to determine the amount of orthophosphate removed at 30, 45, 65, and 80°C (Tables 3 and 4).

ADSORPTION OF ORTHOPHOSPHATE: To attempt to determine whether the orthophosphate was removed by being adsorbed onto the large surface area of the fly ash, the amount of orthophosphate removed by a given amount of fly ash was fitted to Freundlich and Langmuir adsorption isotherms. The procedure used was to take 100 ml of various orthophosphate solutions containing from 0.200 to 1.200 ppm P and add the same amounts of Gascoyne fly ash--25 and 30 mg--to each flask. (A trial using 35 mg of fly ash per 100 ml resulted in the removal of all orthophosphate from all samples and was discarded.) The flasks were placed in an 80°C water bath and shaken at 180 vibrations per minute for 30 minutes. After filtration through a millipore filter the samples were analyzed for orthophosphate (Table 5).

TABLE 3

GASCOYNE FLY ASH

Mg Fly Ash per 100 ml 1 ppm P Solution	30°C		45°C		65°C		80°C	
	PPM P Remaining	% P Removed	PPM P Remaining	% P Removed	PPM P Remaining	% P Removed	PPM P Remaining	% P Removed
1000	0.01	98.8	0.01	98.8	0.01	98.9	0.02	98.4
500	0.03	97.5	0.02	98.5	0.02	98.7	0.02	98.4
250	0.04	96.8	0.02	97.7	0.02	98.4	0.03	97.4
100	0.11	90.0	0.05	95.0	0.03	97.2	0.04	96.8
50	0.48	56.2	0.29	73.6	0.17	85.4	0.08	93.6
25	0.58	46.1	0.61	43.6	0.52	54.6	0.43	63.4
10	1.04	3.7	0.99	8.4	0.95	16.6	0.86	27.0
none	1.08	---	1.08	---	1.13	---	1.18	---

TABLE 4

STANTON FLY ASH

Mg Fly Ash per 100 ml 1 ppm P Solution	30°C PPM P Remaining	30°C % P Removed	45°C PPM P Remaining	45°C % P Removed	65°C PPM P Remaining	65°C % P Removed	80°C PPM P Remaining	80°C % P Removed
500	0.04	96.7	0.04	96.8	0.02	97.8	0.03	97.5
100	0.26	76.1	0.22	80.3	0.03	97.4	0.04	96.3
50	0.65	41.0	0.46	57.7	0.29	72.8	0.20	82.4
25	0.88	19.8	0.87	20.9	0.61	42.7	0.52	54.0
10	1.03	6.1	1.01	8.0	0.94	12.2	0.89	22.2
none	1.10	---	1.10	---	1.07	---	1.14	---

TABLE 5

ADSORPTION DATA FOR ORTHOPHOSPHATE REMOVAL USING FLY ASH

Mg Fly Ash	PPM P in Original Solution	PPM P Remaining	PPM P Removed by Fly Ash	$x = \frac{\text{Mg P "Adsorbed"}}{\text{Mg Adsorbing Material}}$
25	0.24	0.05	0.19	7.5×10^{-4}
	0.44	0.08	0.36	1.4×10^{-3}
	0.64	0.14	0.50	2.0×10^{-3}
	0.84	0.21	0.63	2.5×10^{-3}
	1.06	0.28	0.78	3.1×10^{-3}
	1.25	0.58	0.67	2.7×10^{-3}
30	0.22	0.03	0.19	6.4×10^{-4}
	0.41	0.04	0.37	1.2×10^{-3}
	0.62	0.06	0.56	1.8×10^{-3}
	0.82	0.09	0.73	2.4×10^{-3}
	1.03	0.13	0.90	3.0×10^{-3}
	1.22	0.27	0.95	3.2×10^{-3}

According to the Freundlich isotherm expression[13] $x = kc^n$ where x is the grams of phosphorus adsorbed per gram of adsorbing material, c is the concentration of phosphorus in the original solution (g/l), n is a constant ranging from 0.1 to 0.5, and k is another constant. Rearrangement of the above equation gives $\log x = n\log c + \log k$. A plot of log c vs. log x using the data in Table 5 gave a nearly straight line except at the highest phosphorus concentrations (Fig. 3, Table 6).

TABLE 6

FREUNDLICH ADSORPTION ISOTHERM FOR ORTHOPHOSPHATE REMOVAL

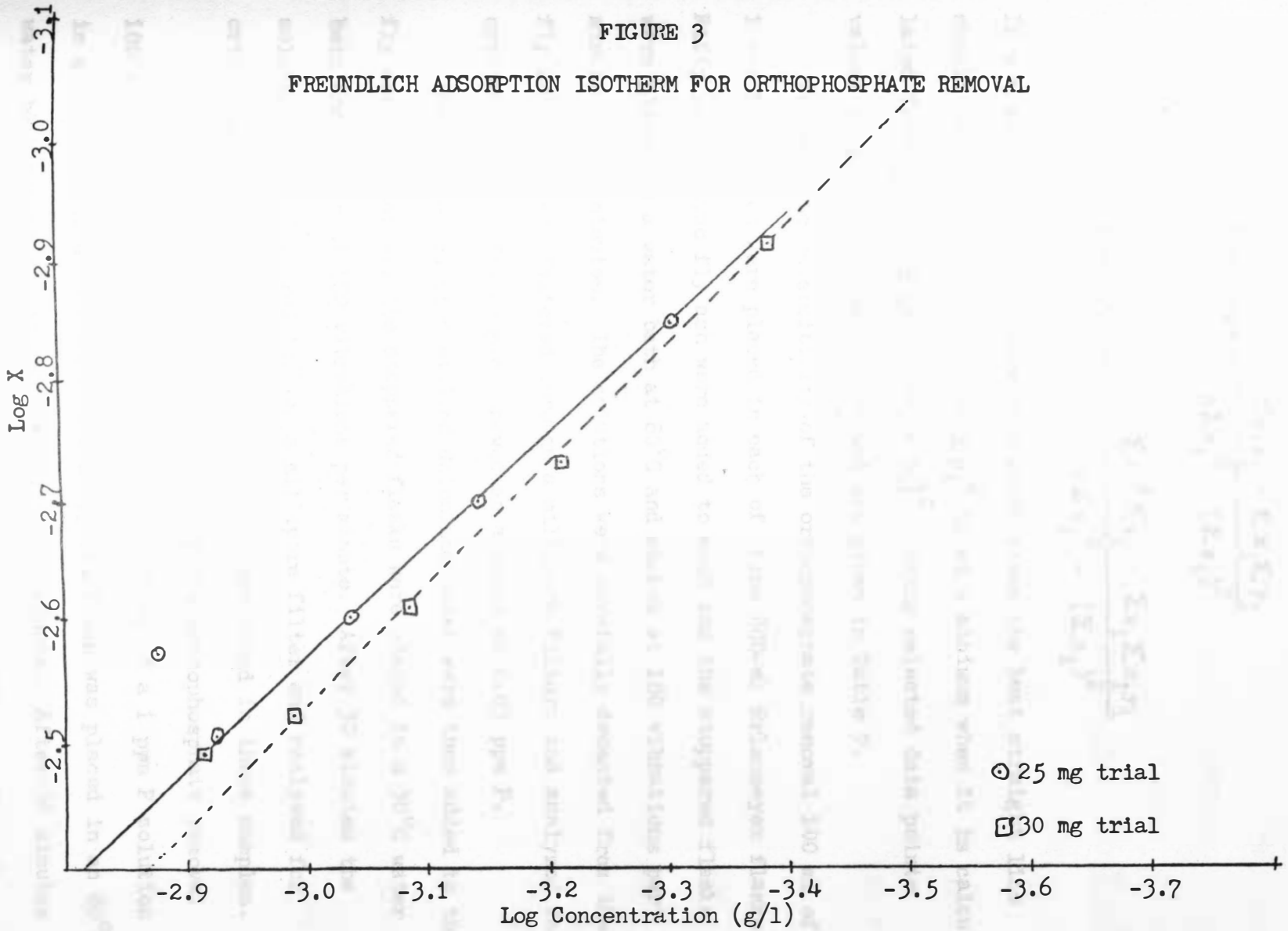
Mg Fly Ash	Log k (intercept)	k	n (slope)
25	0.380	2.40	0.96
30	0.420	2.63	0.98

The Langmuir adsorption isotherm for a species which is associated in the adsorbed phase[14] is $c^n/x = 1/a + c^n b/a$ where c and x are as given above; a, b, and n are constants. To plot the data, the equation is rearranged to give $1/x = 1/ac^n + b/a$. The degree of association of the adsorbed species, n, is adjusted to give the best straight line.

Using values of n = 0.5, 0.9, 1.0, 1.1, 1.5, 2.0, 2.5, and 3.0, $1/c^n$ was calculated. Then a least-squares refinement procedure was used to calculate the slope and the intercept for each set of data at each value of n. Using the following formulas the values of m and b were calculated for each value of n in both trials A and B.

FIGURE 3

FREUNDLICH ADSORPTION ISOTHERM FOR ORTHOPHOSPHATE REMOVAL



$$m = \text{slope} = \frac{n\Sigma y_i x_i - \Sigma x_i \Sigma y_i}{n\Sigma x_i^2 - (\Sigma x_i)^2}$$

$$b = \text{intercept} = \frac{\Sigma x_i^2 \Sigma y_i - \Sigma x_i \Sigma x_i y_i}{n\Sigma x_i^2 - (\Sigma x_i)^2}$$

If $y = mx + b$ then the value of n which gives the best straight line should be that value of n where $\Sigma \rho_i^2$ is at a minimum when it is calculated from $\Sigma \rho_i^2 = \Sigma [y_i - (mx_i + b)]^2$. Using selected data points values of $\Sigma \rho_i^2$ were calculated and are given in Table 7.

To test the reversibility of the orthophosphate removal 100 ml of 1 ppm P solution were placed in each of three 200-ml Erlenmeyer flasks. Fifty mg Gascoyne fly ash were added to each and the stoppered flasks were placed in a water bath at 80°C and shaken at 180 vibrations per minute for 30 minutes. The solutions were carefully decanted from the fly ash residues, filtered through a millipore filter, and analyzed for orthophosphate. The samples showed an average of 0.03 ppm P.

One hundred ml of distilled deionized water were then added to the fly ash residues and the stoppered flasks were placed in a 30°C water bath and shaken at 180 vibrations per minute. After 30 minutes the solutions were filtered through a millipore filter and analyzed for orthophosphate. An average of 0.43 ppm P was found in these samples.

To further test the reversibility of the orthophosphate removal 100 mg of Gascoyne fly ash were added to 500 ml of a 1 ppm P solution in a 1-liter Florence flask. The stoppered flask was placed in an 80°C water bath and shaken at 180 vibrations per minute. After 30 minutes approximately 30 ml of the solution were removed, filtered through a

TABLE 7

LANGMUIR ADSORPTION ISOTHERM FOR ORTHOPHOSPHATE REMOVAL

Trial	Mg of Fly Ash	n = Degree of Association	m = Slope	b = Intercept	$\Sigma \rho i^2$
A	25	0.5	22.7	-386	238
		0.9	0.669	2.1	16.1
		1.0	0.286	52.5	26.5
		1.1	0.125	91.7	57.2
		1.5	4.77×10^{-3}	194	384
		2.0	7.68×10^{-5}	305	426
B	30	0.5	26.5	-510	952
		0.9	0.761	-43.2	130
		1.0	0.327	13.2	50.3
		1.1	0.141	60.1	15.9
		1.5	5.28×10^{-3}	183	185
		2.0	9.32×10^{-5}	267	1153

millipore filter, and analyzed for orthophosphate. The remaining phosphate-fly ash mixture was placed in a 50°C water bath and shaken at 180 vibrations per minute for 3 hours. After this time another 30 ml sample was withdrawn and analyzed for orthophosphate. Finally the flask was placed in a 30°C water bath, shaken for another 3 hours at 180 vibrations per minute, and the resulting solution filtered and analyzed for orthophosphate (Table 8).

TABLE 8

REVERSIBILITY OF ORTHOPHOSPHATE REMOVAL

Temperature (°C)	Time (hours)	Average PPM P Remaining in Solution
80	0.5	0.40
50	3.0	0.34
30	3.0	0.38

From the data in Table 8 it appeared that the system had not reached equilibrium after 30 minutes. To test the amount of time required for maximum orthophosphate removal the following procedures were used:

A) One hundred mg of Gascoyne fly ash were added to 500 ml of 1 ppm P solution in a 1-liter Florence flask. The solutions were placed in a water bath and shaken at 180 vibrations per minute. At the times indicated, approximately 30 ml of solution were removed, filtered through a millipore filter, and analyzed for orthophosphate. This

procedure was carried out at 30 and 80°C.

B) Twenty mg of Gascoyne fly ash were added to 100 ml of 1 ppm P solution in each of six 200-ml Erlenmeyer flasks and placed in a 30°C water bath and shaken at 180 vibrations per minute. At the times indicated one flask was removed from the water bath; the solution was filtered through a millipore filter and analyzed for orthophosphate. This same procedure was used at 80°C using 10 mg of Gascoyne fly ash per 100 ml of 1 ppm P solution (Table 9).

TABLE 9

AMOUNT OF TIME NECESSARY FOR MAXIMUM ORTHOPHOSPHATE REMOVAL

Time in Water Bath (hours)	Average % P Removed (30°C)		Average % P Removed (80°C)	
	Procedure A (100 mg per 500 ml)	Procedure B (20 mg per 100 ml)	Procedure A (100 mg per 500 ml)	Procedure B (10 mg per 100 ml)
0.17	10.6	8.0	60.9	20.4
0.50	10.7	13.0	69.4	21.7
1.0	18.7	22.7	74.4	25.6
3.0	45.2	54.5	81.5	37.5
6.0	60.1	67.2	89.6	56.7

WATER EXTRACTION OF FLY ASH: To test the possibility that the orthophosphate was being removed by a precipitation reaction with one or more of the soluble components of the fly ash the following procedures were used:

A) One thousand mg of Gascoyne fly ash were added to 500 ml of

distilled deionized water in a 1-liter Florence flask. The stoppered flask was placed in a water bath for 24 hours at the temperatures indicated (30 and 80°C) and shaken at 180 vibrations per minute. The water extract was then carefully decanted and 500 ml of 1 ppm P solution were added to the fly ash residue. After 3 more hours in the water bath the solution was analyzed for orthophosphate.

The water extract was filtered through a millipore filter, 50 ml of the extract were added to 50 ml of 1 ppm P solution, and the flasks were placed in the water bath and shaken at 180 vibrations per minute. At the times indicated the flasks were removed, part of the solution was analyzed for orthophosphate immediately and the other part of the solution was filtered through a millipore filter and then analyzed for orthophosphate (Table 10).

B) One hundred mg samples of Gascoyne fly ash were extracted varying numbers of times at 80°C using 100 ml of distilled deionized water for each extraction. A 30-minute time period was used for each extraction with the sample being shaken at 180 vibrations per minute. After the given number of extractions 100 ml of 1 ppm P solution were added to the extracted fly ash residues. The solutions were returned to the water bath for 30 minutes at 80°C, then filtered through a millipore filter, and finally analyzed for orthophosphate (Table 11).

TABLE 10

WATER EXTRACTION OF FLY ASH

Sample	Time in Water Bath (hours)	PPM P Remaining 30°C Without Millipore	30°C After Millipore	80°C Without Millipore	80°C After Millipore
Water extract of fly ash	24	**	0.00	**	0.00
50 ml extract + 50 ml 1 ppm P	none	0.49	0.00	0.50	0.00
	0.17	0.48	0.00	0.47	0.00
	0.50	0.48	0.00	0.46	0.00
	1.0	0.47	0.00	0.44	0.00
	3.0	0.47	0.00	0.40	0.00
Extracted fly ash residue + 500 ml 1 ppm P	3.0	0.36	0.16	0.18	0.00
Original 1 ppm P solution	none	1.00	0.96	1.00	0.96

** Solution was too cloudy to test

TABLE 11

EFFECT OF WATER SOLUBLE PORTION

OF FLY ASH ON ORTHOPHOSPHATE REMOVAL

Number of Water Extractions	% P Removed
none	98.5
1	84.1
3	44.6
5	17.7
9	1.3

X-RAY DIFFRACTION: To determine the compounds present in the fly ash as received, x-ray powder patterns were run on Gascoyne and Big Stone fly ash samples. A Debye-Scherrer x-ray diffraction powder camera was used employing copper $K\alpha$ x-rays with a nickel filter. Exposure times ranged from 6 to 10 hours with an average of 8 hours. In order to reduce the fluorescence due to the iron compounds present a strip of nickel foil was placed around the sample inside the camera.

The following powder patterns are included in this work:

a) Total Gascoyne fly ash (Table 12)

b) Gascoyne fly ash--bromoform extraction: To separate the fly ash into its components, a small amount of fly ash was added to 20 ml of bromoform. The fly ash separated into three layers: the top layer was almost white, the middle layer was gray, and the bottom layer was black. The bromoform was allowed to evaporate and powder patterns were then taken on each layer (Tables 13-15).

c) Gascoyne fly ash--magnetic component: While working with the fly ash it was noted that the black particles were definitely magnetic. Using a magnet, this portion was separated manually from the remainder of the fly ash (Table 16).

d) Gascoyne fly ash--water soluble portion: 200 mg of fly ash were added to 500 ml of water and placed in a water bath at 80°C. The mixture was shaken at 180 vibrations per minute for 5 hours. The solution was filtered through a millipore filter and divided into two portions. One portion was evaporated and the x-ray powder pattern was run on the resulting white powder (Table 17). Sufficient orthophosphate solution was added to the other portion to make it approximately

2 ppm P and the water was then evaporated. The powder pattern of this white powder was also run (Table 18).

e) Big Stone fly ash--bromoform extraction: A small amount of fly ash was added to 25 ml of bromoform and separated into three layers as above. X-ray powder patterns were run on the top and middle layers of this fly ash (Tables 19 and 20).

The d spacings, relative intensities, and hkl values were taken from the X-ray Powder Data File.[15] The index numbers of those compounds identified are: SiO_2, 5-0490; $CaSO_4$, 6-0226; MgO, 4-0829; NaO_2, 6-0500; Fe_3O_4, 19-629; Fe_2O_3, 13-534; $CaCO_3$, 5-0586; χ-Al_2O_3, 4-0880; CaO, 4-0777. For the compounds identified in the following tables all d spacing values with a relative intensity >12 listed in the literature are included.

TABLE 12

TOTAL GASCOYNE FLY ASH

d_{obs}	d_{lit}	Compound	I_{lit}	I_{obs}	hkl
4.25	4.26	SiO_2	35	20	100
3.34	3.343	"	100	100	101
2.09	---	**	--	50	---
1.82	1.817	SiO_2	17	30	112
1.54	1.541	"	15	10	211
1.49	---	**	--	40	---
1.38	1.375	SiO_2	11	10	203

** indicates lines not identified

TABLE 13

GASCOYNE FLY ASH--BROMOFORM EXTRACTION--TOP LAYER

d_{obs}	d_{lit}	Compound	I_{lit}	I_{obs}	hkl
4.270	4.26	SiO_2	35	40	100
3.731	---	**	--	10	---
3.493	3.49	$CaSO_4$	100	10	002,020
3.345	3.343	SiO_2	100	100	101
*	2.967	Fe_3O_4	30	--	220
2.769	2.77	NaO_2	50	30	020
2.677	2.68	NaO_2	100	30	101
2.522	2.532	Fe_3O_4	100	20	311
2.462	2.458	SiO_2	12	20	110
2.395	---	**	--	20	---
2.284	2.282	SiO_2	12	10	102
2.101	2.106	MgO	100	50	200
2.101	2.099	Fe_3O_4	20	50	400
*	1.93	NaO_2	30	--	121
1.819	1.817	SiO_2	17	40	112
1.695	1.69	NaO_2	12	10	130,220
1.614	1.616	Fe_3O_4	30	5	511
1.546	1.541	SiO_2	15	30	211
1.489	1.489	MgO	52	50	220
1.489	1.485	Fe_3O_4	40	50	440
1.380	1.375	SiO_2	11	40	203

* indicates lines missing on film

** indicates lines not identified

TABLE 14

GASCOYNE FLY ASH--BROMOFORM EXTRACTION--MIDDLE LAYER

d_{obs}	d_{lit}	Compound	I_{lit}	I_{obs}	hkl
4.322	4.26	SiO_2	35	5	100
3.681	3.66	Fe_2O_3	25	10	012
3.496	3.49	$CaSO_4$	100	55	002,020
3.339	3.343	SiO_2	100	70	010
2.959	2.967	Fe_3O_4	30	20	220
2.842	2.849	$CaSO_4$	35	45	210
2.690	2.69	Fe_2O_3	100	50	104
2.515	2.51	Fe_2O_3	50	100	110
2.515	2.532	Fe_3O_4	100	100	311
2.202	2.208	$CaSO_4$	20	10	212
2.202	2.201	Fe_2O_3	30	10	113
2.094	2.086	$CaSO_4$	10	10	113
2.094	2.099	Fe_3O_4	20	10	400
*	1.838	Fe_2O_3	40	--	024
1.819	1.817	SiO_2	17	10	112
1.743	1.748	$CaSO_4$	10	10	040
1.692	1.690	Fe_2O_3	60	10	116
1.611	1.616	Fe_3O_4	30	10	511
1.541	1.541	SiO_2	15	5	211
1.482	1.484	Fe_2O_3	35	70	214
1.482	1.485	Fe_3O_4	40	70	440
1.453	1.452	Fe_2O_3	35	15	330
1.376	1.375	SiO_2	11	10	203

* indicates lines missing on film

TABLE 15

GASCOYNE FLY ASH--BROMOFORM EXTRACTION--BOTTOM LAYER

d_{obs}	d_{lit}	Compound	I_{lit}	I_{obs}	hkl
2.962	2.967	Fe_3O_4	30	40	220
2.694	2.69	Fe_2O_3	100	10	104
2.527	2.532	Fe_3O_4	100	100	311
2.093	2.099	"	20	30	400
1.711	1.715	"	10	10	422
1.614	1.616	"	30	50	511
1.482	1.485	"	40	80	440

TABLE 16

GASCOYNE FLY ASH--MAGNETIC COMPONENT

d_{obs}	d_{lit}	Compound	I_{lit}	I_{obs}	hkl
2.959	2.967	Fe_3O_4	30	25	220
2.523	2.532	"	100	100	311
2.094	2.099	"	20	25	400
1.707	1.715	"	10	15	422
1.613	1.616	"	30	40	511
1.481	1.485	"	40	60	440
1.278	1.281	"	10	10	533

TABLE 17

GASCOYNE FLY ASH--WATER SOLUBLE PORTION

d_{obs}	d_{lit}	Compound	I_{lit}	I_{obs}	hkl
4.969	---	**	--	10	---
3.883	3.86	$CaCO_3$	12	10	102
3.043	3.035	"	100	100	104
2.629	---	**	--	20	---
2.501	2.495	$CaCO_3$	14	20	110
2.287	2.285	"	18	40	113
2.097	2.095	"	18	30	202
1.924	1.913	"	17	40	108
1.879	1.975	"	17	40	116

TABLE 18

GASCOYNE FLY ASH--WATER SOLUBLE PORTION PLUS ≈2 PPM P

d_{obs}	d_{lit}	Compound	I_{lit}	I_{obs}	hkl
3.846	3.86	$CaCO_3$	12	10	102
3.466	---	**	--	10	---
3.043	3.035	$CaCO_3$	100	100	104
2.493	2.495	"	14	40	110
2.288	2.285	"	18	40	113
2.097	2.095	"	18	40	202
1.913	1.913	"	17	40	108
1.876	1.875	"	17	40	116
1.605	1.604	"	8	10	212

** indicates lines not identified

TABLE 19

BIG STONE FLY ASH--BROMOFORM EXTRACTION--TOP LAYER

d_{obs}	d_{lit}	Compound	I_{lit}	I_{obs}	hkl
4.276	4.26	SiO_2	35	80	100
3.875	3.87	$CaSO_4$	6	5	111
3.750	---	**	--	30	---
3.500	3.49	$CaSO_4$	100	100	002,020
3.354	3.343	SiO_2	100	100+	101
2.957	2.967	Fe_3O_4	30	5	220
2.864	2.849	$CaSO_4$	35	30	210
2.784	2.778	CaO	34	20	111
2.685	2.69	Fe_2O_3	100	30	104
2.530	2.532	Fe_3O_4	100	20	311
2.470	2.473	$CaSO_4$	8	20	022
2.470	2.458	SiO_2	12	20	110
2.406	2.40	Al_2O_3	40	20	311
2.406	2.405	CaO	100	20	200
2.338	2.328	$CaSO_4$	20	20	202,220
2.290	2.282	SiO_2	12	20	102
2.215	2.208	$CaSO_4$	20	20	212
2.110	2.11	Al_2O_3	30	80	321
2.110	2.099	Fe_3O_4	20	80	400
2.110	2.106	MgO	100	80	200
1.986	1.98	Al_2O_3	20	10	400

Continued on page 29

TABLE 19

BIG STONE FLY ASH--BROMOFORM EXTRACTION--TOP LAYER

d_{obs}	d_{lit}	Compound	I_{lit}	I_{obs}	hkl
Continued from page 28					
1.986	1.993	$CaSO_4$	6	10	301
1.940	---	**	--	5	---
1.872	1.869	$CaSO_4$	16	10	230
1.825	1.817	SiO_2	17	60	112
1.752	1.749	$CaSO_4$	12	10	004
1.697	1.701	CaO	45	10	220
1.679	---	**	--	5	---
1.652	1.648	$CaSO_4$	14	10	232
1.548	1.541	SiO_2	15	30	211
1.492	1.485	Fe_3O_4	40	70	440
1.492	1.490	$CaSO_4$	6	70	214
1.492	1.489	MgO	52	70	220
1.381	1.39	Al_2O_3	100	50	440
1.381	1.375	SiO_2	11	50	203
1.218	1.216	MgO	12	10	222
1.204	---	**	--	10	---
1.187	---	**	--	10	---

** indicates lines not identified

TABLE 20

BIG STONE FLY ASH--BROMOFORM EXTRACTION--MIDDLE LAYER

d_{obs}	d_{lit}	Compound	I_{lit}	I_{obs}	hkl
3.493	3.49	$CaSO_4$	100	30	002,020
3.338	3.343	SiO_2	100	30	101
*	2.967	Fe_3O_4	30	--	220
2.848	2.849	$CaSO_4$	35	20	210
2.761	2.77	NaO_2	50	20	020
2.667	2.68	NaO_2	100	60	101
2.521	2.532	Fe_3O_4	100	20	311
*	2.328	$CaSO_4$	20	--	202,220
2.209	2.208	$CaSO_4$	20	10	212
2.103	2.106	MgO	100	100	200
*	2.099	Fe_3O_4	20	--	400
1.925	1.93	NaO_2	30	20	121
1.754	1.749	$CaSO_4$	12	10	004
1.694	1.69	NaO_2	12	10	130,220
1.613	1.616	Fe_3O_4	30	10	511
1.490	1.485	Fe_3O_4	40	90	440
1.490	1.489	MgO	52	90	220
1.382	---	**	--	10	---
1.277	1.281	Fe_3O_4	10	10	533
1.218	1.216	MgO	12	20	222

* indicates lines missing on film

** indicates lines not identified

pH MEASUREMENTS: The effect of fly ash on the pH of standard phosphate solutions and on lake water samples was studied by adding various amounts of fly ash (0-500 mg) to 100 ml of liquid sample. Standard 1 ppm P solutions and lake water samples from Big Stone Lake, South Dakota, were tested. The flasks were placed in a water bath at the temperatures indicated and shaken at 180 vibrations per minute for 30 minutes. After the solutions had cooled to room temperature the pH was measured using a Beckman pH meter (Tables 21 and 22).

TABLE 21

EFFECT OF FLY ASH ON pH OF STANDARD PHOSPHATE SOLUTIONS

Mg Stanton Fly Ash per 100 ml Standard Phosphate Solution	pH	
	65°C	80°C
500	10.8	11.0
100	10.3	10.5
50	9.8	10.0
25	9.6	9.7
10	8.9	9.3
none	7.0	7.4

TABLE 22

EFFECT OF FLY ASH ON pH OF LAKE WATER SAMPLES AT 80°C

Mg Gascoyne Fly Ash per 100 ml Big Stone Lake Water Sample	pH Water Sample #1	Water Sample #2
500	9.4	9.2
100	8.4	8.5
50	8.4	8.5
25	8.5	8.5
10	8.5	8.5
none	8.3	8.5

ORTHOPHOSPHATE REMOVAL FROM WASTEWATER: To test the ability of fly ash to remove orthophosphate from wastewater, a sample of wastewater was obtained from the Volga, South Dakota, wastewater treatment pond. One hundred ml samples of wastewater were transferred to 200-ml Erlenmeyer flasks and fly ash samples (100-500 mg) were added. The flasks were placed in a 30°C water bath and shaken for 24 hours at 180 vibrations per minute. The samples were filtered through a millipore filter and analyzed for orthophosphate (Table 23).

TABLE 23

ORTHOPHOSPHATE REMOVAL FROM WASTEWATER

Fly Ash Used	Mg Fly Ash per 100 ml Sample	Average PPM P Remaining	% P Removed
Gascoyne	100	0.56	75.3
	300	0.29	87.2
	500	0.16	92.7
Big Stone	100	0.70	68.9
	300	0.19	91.7
	500	0.10	95.6
Filtered Wastewater	none	2.27	---

To test the hypothesis that the orthophosphate was being removed by a precipitation reaction with calcium oxide the following test was done: Assuming that the fly ash contained approximately 15% calcium oxide, various amounts of CaO (15-75 mg) were added to 100 ml samples of wastewater. The solutions were placed in a water bath at 30°C and shaken at 180 vibrations per minute for times ranging from 1 to 24 hours, filtered through a millipore filter, and analyzed for orthophosphate concentration (Table 24).

TABLE 24

ORTHOPHOSPHATE REMOVAL USING CALCIUM OXIDE

Sample Number	Mg CaO per 100 ml Wastewater	Time in Water Bath	Ml Sample Analyzed
1			5
2	45	1 hr	10
3			20
4			5
5	45	4 hr	10
6			20
7			5
8	45	24 hr	10
9			20
10			5
11	15	24 hr	10
12			20
13			5
14	45	24 hr	10
15			20
16			5
17	75	24 hr	10
18			20

All of the orthophosphate had been removed from all samples except samples 10-12 which showed an average of 0.15 ppm P remaining.

RESULTS

CONDITIONS FOR MAXIMUM ORTHOPHOSPHATE REMOVAL: The results (Tables 3 and 4) show little variation in orthophosphate removal based on the type of fly ash used. Both the Stanton and Gascoyne fly ash samples removed approximately equivalent amounts of orthophosphate if other factors were held constant.

The amount of orthophosphate removed from the solution shows a direct relationship to the amount of fly ash added. The addition of 10 mg of fly ash per 100 ml of 1 ppm P solution showed an average of only 13% removal of the orthophosphate present. Increasing the fly ash samples to 100 mg per 100 ml of 1 ppm P solution resulted in an average of 90% removal of the orthophosphate originally present. Further increases in the amount of fly ash added to 250, 500, and 1000 mg samples of fly ash per 100 ml of 1 ppm P solution showed an average of 97% removal of the orthophosphate present.

Elevated temperatures greatly increase the amount of orthophosphate removed from solutions; 50 mg of Stanton fly ash per 100 ml of 1 ppm P solution removed only 41% of the orthophosphate at 30°C but removed 82% at 80°C.

For all of these trials the fly ash samples and orthophosphate solutions were in contact for 30 minutes. As seen later in this work that was not sufficient time for maximum orthophosphate removal but still does show the general trends for any variation due to the type of fly ash, size of fly ash sample, and temperature of the solutions.

ADSORPTION OF ORTHOPHOSPHATE: Since fly ash is such a fine powder with a very large surface area it may be possible that the orthophosphate is removed by adsorption onto the surface of the fly ash. Plotting the data obtained (Table 5) according to the Freundlich adsorption equation gives a nearly straight line (Fig. 3) except at the highest orthophosphate concentrations which may be the result of saturation of the adsorption sites on the fly ash.

However, in using the Langmuir adsorption equation the results from the least-squares refinement procedure are difficult to interpret (Table 7). The value of n which gives the best least-squares fit should be the degree of association of the adsorbed species. In Trial A $\Sigma \rho_i^2$ reached a minimum for n equal to 0.9 and for Trial B the lowest $\Sigma \rho_i^2$ value occurred when n was equal to 1.1.

In order for either the Freundlich or the Langmuir adsorption isotherms to be applicable, the process must be an equilibrium process. Since orthophosphate removal is increased at elevated temperatures, then, if it is an equilibrium process, some of the orthophosphate should go back into solution if the temperature is lowered.

The removal of the orthophosphate is found to be reversible; 50 mg of fly ash in 100 ml of 1 ppm P solution at 80°C showed 0.03 ppm P remaining after 30 minutes. After 30 minutes contact time distilled water which was added to the fly ash residue at 30°C showed 0.43 ppm P. However, further testing of the reversibility in going from 80°C to 50°C and 30°C after longer time intervals indicates that equilibrium has apparently not yet been reached after the initial 30 minute time period (Table 8).

The tests that were then used to determine the amount of time necessary for maximum orthophosphate removal show that the amount removed increases significantly as the time is increased up to 6 hours at both of the temperatures that were used (Table 9).

The above results tend to cast doubt on the conclusions that may be drawn from the Freundlich and Langmuir adsorption work since all of that data were taken when the system had not yet reached equilibrium. The following results also eliminate adsorption as the single factor in orthophosphate removal.

WATER EXTRACTION OF FLY ASH: The fly ash was extracted with water for 24 hours. This water soluble portion shows no orthophosphate present; thus it is assumed that there are no water soluble phosphate compounds present in the original fly ash. Addition of this water soluble portion of the fly ash to an equal amount of 1 ppm P solution gave a resulting solution containing 0.50 ppm P. Analysis of these solutions shows this to be true. However, if the solutions were filtered through a millipore filter, no orthophosphate remained. Thus there must be some soluble component in the fly ash which reacts with the orthophosphate to form a very fine precipitate which is removed by the millipore filter. As seen in Table 10 the amount of orthophosphate remaining in the solutions slowly decreases as the time in the water bath increases. One possible explanation is that the fine precipitate was digested to form larger particles which then precipitated out of solution. This is further supported by the 80°C trial compared to the 30°C trial; the higher temperature would be more conducive to digestion of the solid.

The original orthophosphate solution was also passed through the millipore filter; this process removed 0.04 ppm P which is not significant compared to the amount of orthophosphate removed above. The removal of orthophosphate then must be due, at least in part, to the formation of a fine precipitate which is removed by filtration through the millipore filter.

In trying to determine whether the water soluble portion of the fly ash had any effect on the ability to remove orthophosphate the results show that as the number of water extractions increased the ability of the fly ash residues to remove orthophosphate greatly decreased (Table 11). After 9 water extractions the remaining fly ash residue could remove only 1.3% of the orthophosphate compared to a 98.5% removal for the original fly ash under the same conditions.

X-RAY DIFFRACTION: A typical analysis of fly ash (Table 1) indicates the elements present in the fly ash but does not indicate the nature of the compounds that are present in the fly ash as received. The crystalline components in the fly ash as received were identified using x-ray diffraction.

The total Gascoyne fly ash powder pattern (Table 12) shows that the major constituent is SiO_2. The two lines on this film that were not caused by the SiO_2 are identified on later films.

The bromoform extractions were based on the relative densities of the compounds present in the fly ash (Table 25). The density of bromoform is 2.89 g/cm^3.

TABLE 25

RELATIVE DENSITIES OF COMPOUNDS FOUND IN FLY ASH

Compound	Name	Density[16] (g/cm^3)
SiO_2	silicon dioxide (alpha quartz)	2.66
$CaCO_3$	calcium carbonate (calcite)	2.71
NaO_2	sodium superoxide	---
$CaSO_4$	calcium sulfate (anhydrite)	2.96
CaO	calcium oxide (lime)	3.25-3.38
MgO	magnesium oxide (periclase)	3.58
χ-Al_2O_3	chi aluminum oxide (chi alumina)	3.5-3.9
Fe_3O_4	iron oxide (magnetite)	5.18
Fe_2O_3	iron (III) oxide (hematite)	5.24

The top layer resulting from the bromoform extraction of the Gascoyne fly ash (Table 13) contains SiO_2 as the major component and lesser amounts of $CaSO_4$, Fe_3O_4, NaO_2, and MgO. The possibility of having NaO_2 present in the fly ash seems rather remote but according to Cotton and Wilkinson,[17] "Although sodium normally gives Na_2O_2 it will take up further oxygen at elevated pressures and temperatures to form NaO_2." It should be noted that the observed relative intensities of the lines may not always coincide with the literature values since a mixture was analyzed. Several of the less intense lines from some of the compounds were not seen on the film and also several of the less intense lines on the film could not be identified. This would indicate that there may be other crystalline components in the fly ash which are

present in smaller quantities.

The middle layer of the bromoform extraction of the Gascoyne fly ash (Table 14) shows the following compounds present: $CaSO_4$, Fe_2O_3, Fe_3O_4, and a smaller amount of SiO_2.

The bottom layer from the bromoform extraction (Table 15) contains only the two heaviest compounds, Fe_3O_4 and smaller amounts of Fe_2O_3.

The magnetic separation yielded the magnetic component (Table 16) which is Fe_3O_4.

The main component of the water soluble portion of the Gascoyne fly ash (Table 17) is Ca^{2+} which was identified by precipitation as $CaCO_3$. Addition of orthophosphate solution to a portion of the water soluble extract still showed Ca^{2+} precipitated as $CaCO_3$ (Table 18). If any $Ca_3(PO_4)_2$ was formed the quantity was too small to detect using x-ray diffraction.

The top layer resulting from the bromoform extraction of Big Stone fly ash (Table 19) shows the same compounds as the Gascoyne fly ash, SiO_2, $CaSO_4$, Fe_3O_4, and MgO, but no lines consistent with the presence of NaO_2 were observed. Additional compounds present are CaO, Fe_2O_3, and Al_2O_3.

In the middle layer from the bromoform extraction of Big Stone fly ash (Table 20) the NaO_2 is again present along with $CaSO_4$, Fe_3O_4, SiO_2, and MgO.

pH MEASUREMENTS: The addition of fly ash to water will raise the pH (Table 21) perhaps due to the dissolution of the calcium and sodium compounds present in the fly ash. The pH changes are much greater in

the standard phosphate samples. The addition of 1 mg of fly ash per ml of solution resulted in an average increase of 3.1 pH units. However, the natural buffer system present in lake water can decrease the basic effect of the fly ash; addition of 1 mg of fly ash per ml of lake water showed only a very slight change in pH. The buffer capacity of the lake water was exceeded with the addition of 5 mg of fly ash per ml of lake water.

ORTHOPHOSPHATE REMOVAL FROM WASTEWATER: The addition of 100 mg of fly ash to 100 ml of wastewater removed at least 68% of the 2.27 ppm P originally present (Table 23). When 500 mg of fly ash was added to 100 ml of sample up to 95% of the orthophosphate was removed.

If it is assumed that the fly ash contains 15% CaO then the addition of 15-75 mg of CaO to 100 ml of wastewater should give the same results as in the trials above provided that the orthophosphate is being removed by a precipitation reaction with some form of calcium ion in solution. The results from the addition of this amount of CaO to the wastewater samples show that nearly all of the orthophosphate was removed from all samples (Table 24). These findings may be the result of the following reactions. If this type of reaction is occurring it can be seen from the following calculations that there would be no detectable orthophosphate remaining in the solution.

$$CaO + H_2O \longrightarrow Ca(OH)_2 \qquad (1)$$

$$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2\,OH^{1-} \qquad (2)$$

$$K_{sp}{}^{18} = [Ca^{2+}][OH^{1-}]^2 = 1.3 \times 10^{-6}$$

In a saturated solution of CaO (solubility of CaO = 70 mg/100 ml at 80°C):

let $X = [Ca^{2+}]$, then $[OH^{1-}] = 2X$

$K_{sp} = X\,(2X)^2 = 1.3 \times 10^{-6}$

$X = 6.9 \times 10^{-3}$ M $= [Ca^{2+}]$

$$Ca_3(PO_4)_2 \rightleftharpoons 3\,Ca^{2+} + 2\,PO_4^{3-} \qquad (3)$$

$K_{sp}^{19} = [Ca^{2+}]^3 [PO_4^{3-}]^2 = 1.3 \times 10^{-32}$

If $[Ca^{2+}] = 6.9 \times 10^{-3}$ and let $X = [PO_4^{3-}]$

then $(6.9 \times 10^{-3})^3\,(X)^2 = 1.3 \times 10^{-32}$

$X = 2 \times 10^{-13}$ M $= [PO_4^{3-}]$

2×10^{-13} M $PO_4^{3-} = 2 \times 10^{-13}$ moles P/liter

2×10^{-13} moles P/liter x 31 g P/mole $= 6.2 \times 10^{-12}$ g P/liter

6.2×10^{-12} g P/liter $= 6.2 \times 10^{-9}$ mg P/liter

$= 6.2 \times 10^{-9}$ ppm P remaining in solution

However, in the fly ash not all of the calcium is present in the form of CaO. $CaSO_4$ and perhaps other calcium compounds are present. This will influence the Ca^{2+} concentration in solution. Also in using the fly ash samples the pH of the solution increases upon the addition of fly ash due to dissolution of sodium and calcium compounds and perhaps other soluble hydroxides which are present. The net result of this would be to decrease the Ca^{2+} concentration according to equation

(2) above. This in turn will result in an increase in the PO_4^{3-} concentration remaining in solution according to equation (3).

In a more basic environment the amount of phosphorus removed will be governed by the formation of hydroxylapatite, $Ca_{10}(PO_4)_6(OH)_2$.

$$K_{sp}^{20} = [Ca^{2+}]^{10}[PO_4^{3-}]^6[OH^{1-}]^2 = 1 \times 10^{-90}$$

It has also been shown that fly ash contains soluble iron compounds[21] and thus the removal of the orthophosphate may be the result, perhaps in part, of the formation of other insoluble phosphate compounds such as iron phosphate or aluminum phosphate.

The exact composition of the precipitate formed was not determined in this work so it may only be speculated that it is the result of a precipitation reaction with the Ca^{2+} in solution. However, it was found that the ability to remove orthophosphate from solution is greatly influenced by the water soluble portion of the fly ash and thus it may be concluded that the orthophosphate removal is not a result of simple adsorption of the orthophosphate onto the surface of the fly ash.

CONCLUSIONS

Fly ash has been shown to be an effective means of eliminating orthophosphate from standard phosphate solutions and from wastewater. Different types of fly ash remove essentially the same amount of orthophosphate. The most efficient removal occurs when the fly ash and the water samples are shaken to allow adequate mixing. The amount of orthophosphate removed steadily increases as the temperature is raised and also increases as the contact time is increased. The removal of the very fine fly ash particles from solutions prior to analysis for orthophosphate was most efficiently accomplished by filtration through a millipore filter.

The data obtained could be correlated to the Freundlich adsorption isotherm but not to the Langmuir adsorption isotherm. The experimental data was taken when the systems had not yet reached equilibrium so the results are speculative at best.

It was shown, however, that the removal of orthophosphate is the result, perhaps in part, of a precipitation reaction with some soluble component(s) present in the fly ash. The exact composition of the precipitate formed was not determined in this work but it is proposed that it is the result, in part, of a reaction with the calcium ion in solution. The composition of the precipitate formed will depend on the pH of the solution.

The x-ray diffraction results show the major crystalline components present in the fly ash as received to be SiO_2, $CaSO_4$, CaO, Fe_2O_3, Fe_3O_4, χ-Al_2O_3, MgO, and NaO_2.

NOTES

[1]G. F. Lee, in "Phosphorus in Fresh Water and the Marine Environment," S. H. Jenkens and K. J. Ives, Ed., Pergamon Press, New York, 1973, p. 111.

[2]W. Stumm, in "Phosphorus in Fresh Water and the Marine Environment," S. H. Jenkens and K. J. Ives, Ed., Pergamon Press, New York, 1973, p. 131.

[3]J. M. Cohen, in "Nutrients in Natural Waters," H. E. Allen and J. R. Kramer, Ed., John Wiley and Sons, Inc., New York, 1972, p. 358.

[4]Ibid., p. 360.

[5]Ibid., p. 365.

[6]B. Ericsson, in "Phosphorus in Fresh Water and the Marine Environment," S. H. Jenkens and K. J. Ives, Ed., Pergamon Press, New York, 1973, p. 228.

[7]M. W. Tenney and W. F. Echelberger, Jr., "Fly Ash Utilization in the Treatment of Polluted Waters," U. S. Bur. Mines Inform. Cir. 8488, Ash Utilization, Proc. 2nd Ash Utilization Symp., U. S. Dept. of Interior, 1970, p. 237.

[8]O. E. Manz, Civil Engineering Dept., University of North Dakota, personal communication, 1969.

[9]Tenney, p. 239.

[10]W. Beckering, U. S. Energy Research and Development Administration, personal communication, 1975.

[11]F. S. Watanabe and S. R. Olsen, Soil Sci. Soc. Amer. Proc., 29, 677-78(1965).

[12]M. Taras and A. Greenberg, "Standard Methods for the Examination of Water and Wastewater," 13th Ed., American Public Health Association, New York, 1971, pp. 530-32.

[13]G. M. Barrow, "Physical Chemistry," 2nd Ed., McGraw-Hill Book Co., New York, 1966, p. 766.

[14]H. G. Hecht, Chemistry Dept., South Dakota State University, personal communication, 1975.

[15]"X-ray Powder Data File," American Society for Testing Materials, ASTM Special Technical Publication 48-J.

[16]"Handbook of Chemistry and Physics," R. C. Weast, Ed., The Chemical Rubber Co., Cleveland, Ohio, 1973, pp. B64-B139, C369.

[17]F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd Ed., John Wiley and Sons, Inc., New York, 1972, p. 196.

[18]R. E. Dickerson, H. B. Gray, and G. P. Haight, "Chemical Principles," 2nd Ed., W. A. Benjamin, Inc., Menlo Park, Calif., 1974, p. 201.

[19]Ibid., p. 201

[20]Tenney, p. 241.

[21]D. C. Shannon and L. O. Fine, Environ. Sci. Technol., 8, 1026 (1974).

BIBLIOGRAPHY

Barrow, G. M. "Physical Chemistry." 2nd Ed. New York: McGraw-Hill Book Co., 1966.

Beckering, W. U. S. Energy Research and Development Administration, personal communication, 1975.

Burton, J. D. in "Phosphorus in Fresh Water and the Marine Environment." S. H. Jenkens and K. J. Ives, Ed. New York: Pergamon Press, 1973, pp. 291-307.

Cohen, J. M. in "Nutrients in Natural Waters." H. E. Allen and J. R. Kramer, Ed. New York: John Wiley and Sons, Inc., 1972, pp. 353-389.

Cooke, G. W. and Williams, R. J. B. in "Phosphorus in Fresh and the Marine Environment." S. H. Jenkens and K. J. Ives, Ed. New York: Pergamon Press, 1973, pp. 19-33.

Cotton, F. A. and Wilkinson, G. "Advanced Inorganic Chemistry." 3rd Ed. New York: John Wiley and Sons, Inc., 1972.

Dickerson, R. E., Gray, H. B., and Haight, G. P. "Chemicals Principles." 2nd Ed. Menlo Park, Calif.: W. A. Benjamin, Inc., 1974.

Ericsson, B. in "Phosphorus in Fresh and the Marine Environment." S. H. Jenkens and K. J. Ives, Ed. New York: Pergamon Press, 1973, pp. 227-247.

"Handbook of Chemistry and Physics." R. C. Weast, Ed. Cleveland, Ohio: The Chemical Rubber Co., 1973.

Hecht, H. G. Chemistry Dept., South Dakota State University, personal communication, 1975.

Jones, P. H. in "Phosphorus in Fresh and the Marine Environment." S. H. Jenkens and K. J. Ives, Ed. New York: Pergamon Press, 1973, pp. 211-226.

Kemp, A. L. W., Gray, C. B. J., and Mudrochova, A. in "Nutrients in Natural Waters." H. E. Allen and J. R. Kramer, Ed. New York: John Wiley and Sons, Inc., 1972, pp. 251-279.

Kramer, J. R., Herbes, S. E. and Allen, H. E. in "Nutrients in Natural Waters." H. E. Allen and J. R. Kramer, Ed. New York: John Wiley and Sons, Inc., 1972, pp. 51-100.

Lee, G. F. in "Phosphorus in Fresh Water and the Marine Environment." S. H. Jenkens and K. J. Ives, Ed. New York: Pergamon Press, 1973, pp. 111-128.

Manz, O. E. Civil Engineering Dept. University of North Dakota, personal communication, 1969.

Shannon, D. C. and Fine, L. O. Environ. Sci. Technol., 8, 1026(1974).

Stumm, W. in "Phosphorus in Fresh and the Marine Environment." S. H. Jenkens and K. J. Ives, Ed. New York: Pergamon Press, 1973, pp. 131-144.

Taras, M. and Greenberg, A. "Standard Methods for the Examination of Water and Wastewater." 13th Ed. New York: American Public Health Association, 1971.

Tenney, M. W. and Echelberger, W. F., Jr. "Fly Ash Utilization in the Treatment of Polluted Waters." U. S. Bur. Mines Inform. Cir. 8488, Ash Utilization, Proc. 2nd Ash Utilization Symp., U. S. Dept.of Interior, 1970, pp. 237-268.

Watanabe, F. S. and Olsen, S. R. Soil Sci. Soc. Amer. Proc., 29, 677-78(1965).

Williams, J. D. H. and Meyer, T. in "Nutrients in Natural Waters." H. E. Allen and J. R. Kramer, Ed. New York: John Wiley and Sons, Inc., 1972, pp. 281-315.

"X-ray Powder Data File." American Society for Testing Materials, ASTM Special Technical Publication 48-J.